PARTITIONING EFFECTS IN RECRYSTALLIZATION OF SILICON FROM SILICON-METAL SOLUTIONS

E.A. Good, T.H. Wang[1], T.F. Ciszek[1], R.H. Frost[2], M.R. Page[1], and M.D. Landry[1]
1. National Renewable Energy Laboratory, Golden, CO 80401
2. Colorado School of Mines Metallurgical and Materials Engineering Dept., Golden, CO 80401

ABSTRACT

The objective of this work is to investigate various silicon-metal eutectic systems that selectively retain detrimental impurities, such as Ni, Co, Fe, Cr, in the melt so that silicon may be purified. We studied possible interactions in the melt and in the silicon crystal between impurity elements and solvent metals that lead to reduced or enhanced impurity partition relative to the respective silicon-impurity binary systems. Systems such as Al- Si, Cu-Si, and In-Si show promises of reduced impurity incorporations in recrystallized silicon, which are good candidates for further investigation besides Ga-Si, Au-Si, and Ag-Si.

INTRODUCTION

One of the major issues facing PV manufacturers today is the supply and cost of solar-grade silicon (SoG-Si) with low detrimental metal impurity concentrations. As we reported in a previous publication [1], a novel approach to purifying metallurgical grade silicon (MG-Si) in lieu of the conventional distillation of chlorosilanes is silicon-metal solution growth. Figure 1 shows a simple phase diagram of a binary silicon-metal eutectic system. As the temperature is lowered from above the liquidus line, silicon precipitates out along the left axis with a low metal content according to the metal's solubility in silicon at the liquidus/composition interception temperature.

When solidifying silicon from an almost pure silicon melt, impurities contained in the silicon melt also incorporate into the silicon lattice according to their respective impurity-silicon binary solubilities at the silicon melting point. However, if we use some metals as solvents to dissolve silicon, one can recrystallize silicon at a much lower temperature and impurities contained in the silicon-metal solutions will also incorporate at the lowered temperature. The use of a metal solvent dilutes these impurities in MG-Si, thus the incorporation into the recrystallized silicon will be proportionally less. Furthermore, most impurities exhibit retrograde solubility in silicon with peaks around 1300°C. Some of the most harmful elements in metallurgical-grade silicon such as, Ni, Co, Fe, and Cr, have their solubility in silicon decreased by more than one order of magnitude from that at the silicon melting point if the crystallization is done at temperatures below 800°C instead. Many metals form eutectics with silicon at much lower temperatures than the silicon melting point. These include Ag, Al, Au, Cu, Ga, In, Sb, Sn, Zn, etc. One would prefer those of which with low or no detrimental effects on solar cell performances and with moderate slope of the liquidus line to afford fast recrystallization of silicon.

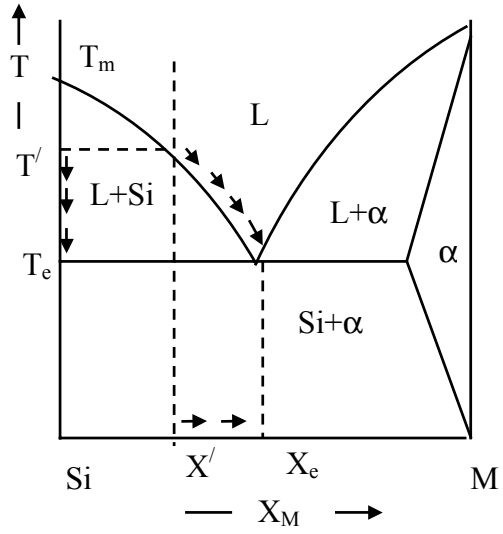

Figure 1 – Simple binary eutectic phase diagram for a silicon-metal system. Arrows illustrate growth along liquidus curve yielding precipitation of Si.

Interactions between an impurity and the metal solvent in a silicon-metal solution could change the impurity's chemical potential, thereby altering its partition coefficient. An attractive interaction retains the impurity in the solution by the solvent, and vice versa. These can be studied by means of the regular solution model in combination with experimental data.

In addition to dilution and interaction effects, a third mechanism could account for the reduced incorporation of some electrically active impurities into the silicon lattice. The law of mass action or Fermi energy level restriction reveals a type of interaction between an ionized impurity and the electrically active solvent element in the recrystallized silicon. This phenomenon could lead to either reduced or enhanced impurity segregation coefficient depending on the impurity's defect energy levels and the silicon Fermi energy level that is determined by incorporation of the solvent metal.

CRYSTAL GROWTH

Bulk crystals of silicon were grown in a 10kHz induction heated furnace with a charge size nearly 300g (Fig. 2). Compositions were selected from phase diagrams for each system such that silicon recrystallization takes place at or around 900°C. Electronic-grade silicon doped with impurities, at levels comparable to MG-Si, was used for precise control of initial impurity contents (e.g. B ~2 x 10^{18} atoms/cc). Kryopolous growth, as described by Brice [5], from (100) seeds yielded single crystal and multicrystalline samples depending on the growth conditions.

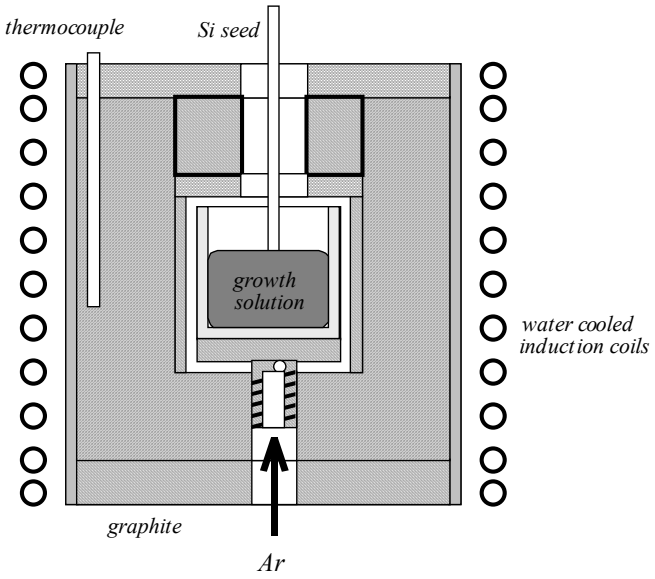

Fig. 2 Experimental setup for recrystallization

Figure 3 - Silicon-aluminum melt and multicrystalline growth

Figure 4 - Single crystal silicon grown from Si-Al

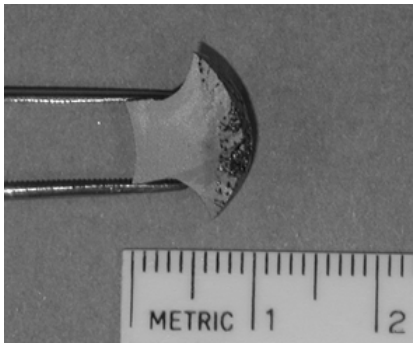

Figure 5 - A longitudinal cross-section of a single crystal silicon sample

INTERACTION IN THE MELT - THE REGULAR SOLUTION MODEL

When solidifying silicon from a Al-Cu-Si ternary solution, the chemical potentials of respective elements in the liquid phase must be equal to those in the solid phase. The chemical potential of individual element is determined by its activity (the ratio of an element's fugacity in the mixture at equilibrium to the fugacity in its pure state), which is the product of activity coefficient and composition

fraction. Using the regular solution model, the interaction parameters between the three components at 1173K are experimentally obtained as, $\Omega^{l}_{SiAl} = 2.430RT$, $\Omega^{l}_{SiCu} = 2.469RT$, $\Omega^{l}_{AlCu} = -0.103RT$. Therefore, the segregation coefficient of Al for growth of silicon from Al-Cu-Si mixture can be derived [2],

$$k_{Al} = \frac{x^s_{Al}}{x^l_{Al}} = \frac{\gamma^l_{Al}}{\gamma^s_{Al}} = \frac{\exp\left[2.430\left(x^l_{Si}\right)^2 - 0.103\left(x^l_{Cu}\right)^2 - 0.142 x^l_{Si} x^l_{Cu}\right]}{8991}.$$

Similarly for Cu, we have:

$$k_{Cu} = \frac{x^s_{Cu}}{x^l_{Cu}} = \frac{\gamma^l_{Cu}}{\gamma^s_{Cu}} = \frac{\exp\left[2.469\left(x^l_{Si}\right)^2 - 0.103\left(x^l_{Al}\right)^2 - 0.064\, x^l_{Si} x^l_{Al}\right]}{3.98\times 10^7}.$$

Because both Ω^{l}_{SiAl} and Ω^{l}_{SiCu} are large positive numbers, Si-Al and Si-Cu interactions are of repulsive nature (with higher heat of mixing). Ω^{l}_{AlCu} is negative, however, implying an attractive interaction between Al and Cu (with lower heat of mixing). Therefore, Cu in the growth solution will not only dilute Al, but also will retain Al in the liquid, thus providing greater control for Al doping. Other Si-metal solvent combinations may be explored in a similar fashion to reduce incorporation of more detrimental impurities using harmless metals as solvents.

INTERACTION IN THE CRYSTAL - THE FERMI ENERGY MODEL

When choosing metal solvents, its conductivity type in silicon is very important. At growth temperature, solvent metal atoms incorporated into the silicon crystal ionize to give a Fermi energy level in silicon (determined by solvent concentration and growth temperature). If an acceptor-type solvent is chosen, other impurities of the same acceptor-type but with energy levels above the Fermi level will not be able to ionize, thus reducing these acceptor impurities' incorporation. Similarly, if the solvent is of donor-type, other donor-type impurities with energy levels below the Fermi Energy will not be able to ionize. The ratio of the impurity solubility from such an impurity-solvent-silicon system to that from an impurity-silicon binary system is given by [3,4]:

for acceptor-type impurities with acceptor-solvent: $\frac{[A]}{[A_{bi}]} = \exp\left(\frac{E_F - E_{imp}}{kT}\right)$,

for donor type impurities with donor-solvent: $\frac{[D]}{[D_{bi}]} = \exp\left(\frac{E_{imp} - E_F}{kT}\right)$,

where the subscript *bi* stands for impurity-silicon binary system, and E_{imp} is the impurity energy level.

The adverse effect is also true. For example, if a solvent is of acceptor type, other impurities of donor-type with energy levels above the Fermi level will be easily ionized to act as donors, so their concentration could be enhanced compared to impurity-silicon binary system.

CHARACTERIZATIONS

Bulk silicon samples grown from eutectic systems: Al-Si, Cu-Si, and In-Si were analyzed for impurity concentrations. Depth profiling by secondary ion mass spectroscopy (SIMS) was preformed on longitudinal cross-sections to achieve true bulk impurity measurements. Figure 6 depicts a SIMS measurement about 50μm into the bulk of a single crystal sample grown from an aluminum melt. From this profile, any non-uniform edge and interface effects can be ignored, as the concentrations appear constant. Table 1 shows that impurity concentrations observed in the crystals grown from Si-metal solutions are quite different from the source levels and from dilution considerations from the intended doping (B, Cu, and Al). The unintended impurities (Mn and Fe) also deviate from even the binary solubilities. Solvents like Ag, Au, and Ga will also be studied for interactions with targeted impurities.

Table 1 – SIMS Bulk Impurity Data for Three Eutectic Systems

	B (intent.)		*Cu (intent.)*		*Al (intent.)*		*Mn (unint.)*		*Fe (unint.)*	
	SIMS	*Source*	*SIMS*	*Melt*	*SIMS*	*Melt*	*SIMS*	*Sol.* [7]	*SIMS*	*Sol.* [7]
Si-Al	2×10^{17}	2×10^{18}	2×10^{15}	2.0×10^{20}	8×10^{18}	*	1×10^{17}	5×10^{14}	2×10^{16}	2×10^{15}
Si-Cu	4×10^{18}	2×10^{18}	1×10^{15}	*	2×10^{16}	8.0×10^{20}	8×10^{14}	7×10^{14}	3×10^{15}	3×10^{15}
Si-In	2×10^{17}	2×10^{18}	1×10^{15}	1.2×10^{21}	7×10^{14}	5.1×10^{20}	3×10^{14}	6×10^{15}	2×10^{15}	1×10^{16}

* Solvent Metal

CONCLUSIONS

Recrystallization from some silicon-metal eutectic systems offers promises for solar-grade silicon feedstock production with several possible purification effects. These effects include: lowering crystallization temperatures, diluting impurity concentrations, attractive impurity-solvent interactions in the solutions, and repulsive impurity-solvent element interactions in the silicon crystal resulting rejection of impurity at the growth interface. Future work will be conducted to systematically determine interaction parameters for all of the major eutectic systems and to complete investigations into the Fermi energy effect on impurity partition.

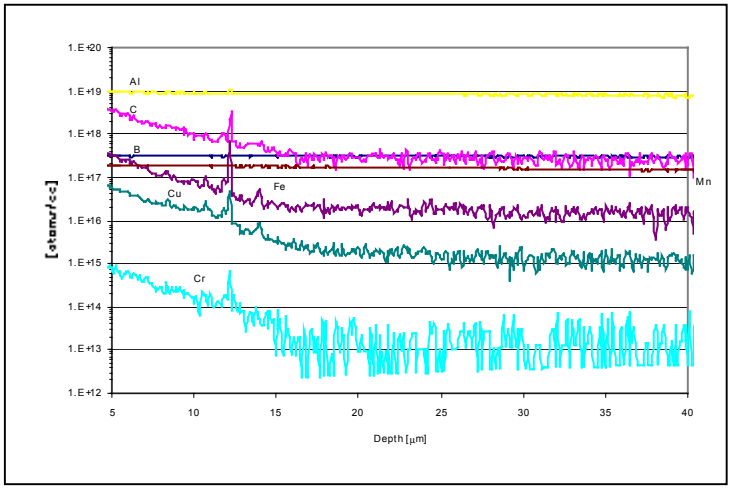

Figure 6 – SIMS impurity data for single crystal silicon grown from Al solution.

ACKNOWLEDGEMENTS

Valuable contributions to this work from the staff of NREL's Silicon Materials Team within the National Center for Photovoltaics are greatly appreciated. Financial support was made possible from a task order agreement between the Colorado School of Mines and the National Renewable Energy Laboratory: No. KCQ-0-30600-20. Robert Reedy and Matthew Young of NREL's measurements and characterization team conducted SIMS analysis.

REFERENCES

[1] T.F. Ciszek, T.H. Wang, M.R. Page, P. Menna, R.E. Bauer, E.A. Good, and J.A. Casey in: *Proceedings of the 11th Workshop on Crystalline Silicon Solar Cell Material and Processes*, Ed: B.L. Sopori (August 2001 NREL/BK-520-30838), pp. 150-154.

[2] T.H. Wang and T.F. Ciszek, "Impurity Segregation in LPE Growth of Silicon from Cu-Al Solutions," *J. of Crystal Growth* **174** (1997) pp.176-181

[3] R.A. Swalin, *Thermodynamics of Solids*, Wiley, New York, 1962, p.305

[4] H.F. Wolf, *Semiconductors*, John Wiley & Sons, New York, 1971 p. 201.W.C. O'mara, R.B.

[5] O.F. Devereux, *Topics in Metallurgical Thermodynamics,* Krieger Publishing Company. Malabar, Florida.1983. pp. 95-107

[6] J.C. Brice, *Crystal Growth Processes*, John Wiley and Sons, New York, 1986, p. 137.

[7] M. Neuberger, S.J. Welles, *Silicon*, DS –162, October 1969.